Catalytic Hydrogenation

DOI: 10.1002/anie.200601366

[Pd(Ar-BIAN)(alkene)]-Catalyzed Highly Chemo-, Regio-, and Stereoselective Semihydrogenation of 1,2-Allenyl Phosphonates and Related Compounds**

Hao Guo, Zilong Zheng, Fei Yu, Shengming Ma,* Alexandre Holuigue, Dorette S. Tromp, Cornelis J. Elsevier,* and Yihua Yu

Allenes are an important class of compounds with many applications in organic chemistry.^[1,2] However, the hydrogenation of allenes is challenging, as there are issues of chemo-, regio-, and stereoselectivity to be addressed (Scheme 1).^[2d] Only a very limited number of studies in this area have been reported, and the selectivity in the reported cases is low.^[3]



Scheme 1. The hydrogenation of allenes.

[*] H. Guo, Z. Zheng, F. Yu, Prof. S. Ma State Key Laboratory of Organometallic Chemistry Shanghai Institute of Organic Chemistry Chinese Academy of Sciences 354 Fenglin Road, Shanghai 200032 (P. R. China) Fax: (+86) 21-6416-7510 E-mail: masm@mail.sioc.ac.cn A. Holuigue, D. S. Tromp, Prof. C. J. Elsevier Van't Hoff Institute for Molecular Sciences University of Amsterdam Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands) Fax: (+31) 20-525-6456 E-mail: elsevier@science.uva.nl Y. Yu Key Laboratory of Optical and Magnetic Resonance Spectroscopy East China Normal University 3663 Zhongshan Road, Shanghai 200062 (P. R. China) [**] The Chinese authors acknowledge financial support from the International Program of the National Natural Science Foundation of China. This research has also been partially funded by the National Research School Combination Catalysis (project number: 2000-14) and by the Universiteit van Amsterdam (grant SAP 2255). We thank Mr. Tao Bai of this group for independently reproducing

bis(arylimino)acenaphthene. Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

representative examples of the work reported herein. Ar-BIAN =

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

InterScience 4997

Communications



One of the authors and co-workers have previously reported the hydrogenation of alkynes catalyzed by [Pd(Ar-BIAN)(alkene)] complexes **1** (Ar-BIAN = bis(arylimino)acenaphthene) to afford Zalkenes in excellent yields with high stereoselectivity.^[4] Herein we report a highly chemo-, regio-, and stereoselective hydrogenation of 1,2allenyl phosphonates to give di- or trisubstituted (Z)-1-alkenyl phosphonates with the same catalysts. Such trisubstituted alkenes are otherwise difficult to obtain.

We first chose the 1,2-allenyl phosphonate **2a** as the model substrate to study the solvent effects of the reaction at 20 °C. In most solvents, such as diethyl ether, dioxane, *N*,*N*-dimethyl formamide, dimethyl sulfoxide, CH_2Cl_2 , CH_3CCl_3 , toluene, CH_3NO_2 , CH_3OH , AcOH, and Et₃N, the hydrogenation did not proceed. Fortunately, when the reaction was conducted in CH_3CN or THF, only the trisubstituted (*Z*)-1-alkenyl phosphonate (*Z*)-**3a** was formed, in excellent yield with excellent chemo-, regio-, and stereoselectivity (Table 1,

Table 1: [Pd(Ar-BIAN)(alkene)]-catalyzed hydrogenation of **2a** under various conditions.^[a,b]

P(OEt) ₂ O 2a	1 mol% 1 H ₂ (1 atm) 20 °C, 24 h	/P(OEt) ₂ (Z)- 3a	
Solvent	Catalyst	<i>T</i> [°C]	Yield [%]
CH ₃ CN	la	20	92
THF	la	20	94
THF	la	30	94
THF	la	50	92
THF	16	20	94
	P(OEt) ₂ 2a Solvent CH ₃ CN THF THF THF THF THF	$\begin{array}{c} & \stackrel{n B u}{\underset{O}{}} & \stackrel{1 \text{ mol} \% \text{ 1}}{\underset{H_2 (1 \text{ atm})}{H_2 (1 \text{ atm})}} \\ \hline & \\ 2a \end{array}$	$\begin{array}{c cccc} & & 1 & mol\% & 1 & & & & & & & \\ \hline & & & & & & & & & \\ P(OEt)_2 & & & & & & & & & \\ \hline & & & & & & & & &$

[a] The reaction was carried out at the temperature stated with **2a** (0.2 mmol) and **1a** or **1b** (1 mol%) in 3 mL of solvent under H_2 (1 atm) for 24 h. [b] The chemo-, regio-, and stereoselectivities were determined by ¹H NMR spectroscopic analysis of the crude reaction product.

entries 1 and 2). As the yield in THF was slightly higher than that in CH₃CN, THF was chosen as the solvent for this reaction. When we increased the reaction temperature, no obvious changes were observed (Table 1, entries 3 and 4). It was also found that the activity of catalyst **1b** was the same as that of **1a** for the hydrogenation of **2a** (Table 1, entry 5).

We next investigated the hydrogenation of various 1,2allenyl phosphonates **2b–j** (Table 2). It was surprising to note that **1a** failed to catalyze the hydrogenation of the methylsubstituted 1,2-allenyl phosphonate **2b** (Table 2, entry 1). As the lack of hydrogenation activity may result from the stronger coordination of the fumaronitrile ligand, we decided to attempt the reaction with palladium complex **1b**, which has a more labile alkene ligand. Indeed, **1b** catalyzed the partial hydrogenation reaction to afford alkene (*Z*)-**3b** in 91 % yield (Table 2, entry 2). Therefore, the same conditions were used



[a] The reaction was carried out at room temperature with **2** (0.2 mmol) and **1b** (1 mol%) in THF (3 mL) under H₂ (1 atm) for 24 h. [b] The chemo-, regio-, and stereoselectivities were determined by ¹H NMR spectroscopic analysis of the crude reaction product. [c] The reaction was conducted with **1a** (1 mol%) as the catalyst. n.r. = no reaction.

for the other substrates. Interestingly, the hydrogenation of **2k** under these conditions gave the (*Z*)-1-alkenyl phosphonate (*Z*)-**3k** in 93% yield as the only product, in which the isolated allylic C=C bond in **2k** had also been hydrogenated, but the conjugated electron-deficient carbon–carbon double bond remained (Scheme 2). The configuration of the C=C bond in the products **3** was determined by analysis of the ¹H-¹H NOESY spectra of (*Z*)-**3i**.



Scheme 2. The hydrogenation of 2k.

The hydrogenation of the 1,3-disubstituted 1,2-allenyl phosphonate **21** and 1,3,3-trisubstituted 1,2-allenyl phosphonates **2m** and **2n** under the conditions indicated in Table 2 was also studied. Compounds (Z)-**31**, (Z)-**3m**, and (Z)-**3n** were formed highly selectively in 92, 95, and 85% yield, respectively (Scheme 3).

On the basis of these and previous results, a mechanism for this reaction is proposed in Scheme 4. The catalytic cycle starts with the loss of the alkene ligand from **1b**. Next, the more electron rich C=C bond in **2** coordinates to palladium in



Scheme 3. The semihydrogenation of 21-n.

Angew. Chem. Int. Ed. 2006, 45, 4997-5000



Scheme 4. A possible mechanism for this reaction.

place of the alkene ligand to form a [Pd(Ar-BIAN)(allene)]complex **5**. In analogy with the mechanism for alkyne hydrogenation studied by one of us and co-workers,^[4c] we propose the heterolytic hydrogen cleavage of **5** to afford the monohydridopalladium complex **6**, which may undergo highly stereoselective hydropalladation to generate the palladium hydride **7a** or **7b** after transfer of the N–H hydrogen atom to Pd.^[5] The final product **3** is produced by reductive elimination from **7a** or **7b**. Meanwhile, the catalytically active [Pd(Ar-BIAN)(allene)] species **5** is regenerated through the interaction of **8** with the starting allene. On the basis of the stereoselectivity observed, we reason that the reaction most likely proceeds via the intermediate **7a**, in which the mutual *trans* orientation of the palladium and phosphonate moieties may determine the stereoselectivity.

This protocol was successfully extended to allenes substituted with other functionalities, namely, the 1,2-allenyl phosphine oxide 9, the 1,2-allenyl sulfone 11, and the 2,3allenoate 13 (Scheme 5). In these cases the semihydrogenation also proceeds with very high chemo-, regio-, and stereoselectivity. Note that toluene should be used as the solvent for the 2,3-allenoate 13.

In conclusion, we have demonstrated a novel, highly chemo-, regio-, and stereoselective [Pd(Ar-BIAN)(alkene)]-catalyzed hydrogenation of 1,2-allenyl phosphonates^[6,7] and other 1,2-allenyl compounds to form di- or trisubstituted (*Z*)-1-alkenyl phosphonates, sulfones, and esters in excellent yields. Further studies in this field are being carried out in our laboratories, including investigations into synthetic applications of the reaction.

Experimental Section

Typical procedure: Catalyst **1b** (1 mg, 0.002 mmol), **2a** (46 mg, 0.2 mmol), and anhydrous THF (3 mL) were added to a Schlenk



Scheme 5. The semihydrogenation of some related compounds.

tube under a nitrogen atmosphere. The nitrogen atmosphere was replaced with a hydrogen atmosphere (1 atm), and the solution was stirred at 20 °C for 24 h. The reaction mixture was then filtered. Evaporation of the solvent and flash chromatography on silica gel (petroleum ether/diethyl ether 1:2) afforded (*Z*)-**3a** (44 mg, 94%) as a liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.24$ (dtq, J = 0.9, 7.2, 50.7 Hz, 1H), 4.13–3.96 (m, 4H), 2.22–2.12 (m, 2H), 2.03–1.98 (m, 3H), 1.48–1.38 (m, 2H), 1.35–1.23 (m, 8H), 0.88 ppm (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75.4 MHz): $\delta = 142.2$ (d, $J_{PC} = 11.8$ Hz), 129.8 (d, $J_{PC} = 10.3$ Hz), 61.0 (d, $J_{PC} = 5.8$ Hz), 35.0 (d, $J_{PC} = 12.1$ Hz), 31.7 (d, $J_{PC} = 3.0$ Hz), 22.2, 16.3 (d, $J_{PC} = 4.4$ Hz), 16.2 (d, $J_{PC} = 2.6$ Hz), 13.8 ppm; ³¹P NMR (121.5 MHz, CDCl₃): $\delta = 21.0$ ppm; IR (neat): $\tilde{\nu} = 1632$, 1444, 1391, 1245, 1026 cm⁻¹; MS: *m/z*: 234 (*M*⁺, 9.87), 44 (100); HRMS (MALDI): *m/z* calcd for C₁₁H₂₃O₃P⁺ [*M*⁺]: 233.1385; found: 234.1400.

Received: April 6, 2006 Published online: June 29, 2006

Keywords: alkenes · allenes · homogeneous catalysis · hydrogenation · palladium

- a) Allenes in Organic Synthesis (Eds.: H. F. Schuster, G. M. Coppola), Wiley, New York, **1984**; b) The Chemistry of Ketenes, Allenes, and Related Compounds, Part 1 (Ed.: S. Patai), Wiley, New York, **1980**; c) Modern Allene Chemistry (Eds.: N. Krause, A. S. K. Hashmi), Wiley-VCH, Weinheim, **2004**.
- [2] For reviews, see: a) K. K. Wang, Chem. Rev. 1996, 96, 207; b) R. Zimmer, C. Dinesh, E. Nandanan, F. Khan, Chem. Rev. 2000, 100, 3067; c) J. Marshall, Chem. Rev. 2000, 100, 3163; d) A. S. K. Hashmi, Angew. Chem. 2000, 112, 3737; Angew. Chem. Int. Ed. 2000, 39, 3590; e) X. Lu, C. Zhang, Z. Xu, Acc. Chem. Res. 2001, 34, 535; f) R. Bates, V. Satcharoen, Chem. Soc. Rev. 2002, 31, 12; g) S. Ma, Handbook of Organopalladium Chemistry for Organic Synthesis (Ed.: E. Negishi), Wiley, New York, 2002, p. 1491; h) L. Sydnes, Chem. Rev. 2003, 103, 1133; i) S. Ma, Acc. Chem. Res. 2003, 36, 701; j) M. Tius, Acc. Chem. Res. 2003, 36, 284; k) L.-L. Wei, H. Xiong, R. P. Hsung, Acc. Chem. Res. 2003, 36, 773; l) L. Brandsma, N. A. Nedolya, Synthesis 2004, 735; m) F. Pan, C. Fu, S. Ma, Chin. J. Org. Chem. 2004, 24, 1168; n) S. Ma, Chem. Rev. 2005, 105, 2829; o) S. Ma in Topics in Organometallic Chemistry (Ed.: J. Tsuji), Springer, Heidelberg, 2005; p) C. J. Elsevier in Houben-Weyl Methoden der Organischen Chemie, Stereoselective Synthesis, Vol. E 21a (Eds.: G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann), Thieme, Stuttgart, 1995, pp. 537-566.

Communications

- [3] a) D. G. Pete, N. Munisamappa, J. Org. Chem. 1961, 26, 3518;
 b) D. Devaprabhakara, P. D. Gardner, J. Am. Chem. Soc. 1963, 85, 648;
 c) J. M. Brown, Chem. Ind. 1963, 1689;
 d) P. Down, J. Chem. Soc. Chem. Commun. 1965, 568;
 e) G. Nagendrappa, D. Devaprabhakara, Tetrahedron Lett. 1970, 4243;
 f) R. Baudouy, J. Gore, Tetrahedron 1975, 31, 383;
 g) L. Crombie, P. A. Jenkins, D. A. Mitchard, J. Chem. Soc. Perkin Trans. 1 1975, 1081;
 h) F. Hammerschmidt, G. Bovermann, K. Bayer, Liebigs Ann. Chem. 1990, 1055.
- [4] a) M. W. Laren, C. J. Elsevier, Angew. Chem. 1999, 111, 3926; Angew. Chem. Int. Ed. 1999, 38, 3715; b) J. W. Sprengers, J. Wassenaar, N. D. Clement, K. J. Cavell, C. J. Elsevier, Angew. Chem. 2005, 117, 2062; Angew. Chem. Int. Ed. 2005, 44, 2026; c) A. M. Kluwer, T. S. Koblenz, T. Jonischkeit, K. Woelk, C. J. Elsevier, J. Am. Chem. Soc. 2005, 127, 15470.
- [5] A. Dedieu, S. Humbel, C. J. Elsevier, C. Grauffel, *Theor. Chem. Acc.* 2004, 112, 305.
- [6] R. Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, *Inorg. Chem.* 1994, 33, 1521.
- [7] H. Altenbach, R. Korff, Tetrahedron Lett. 1981, 22, 5175.